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Diastereoselective Hydrolysis of Asymmetric P–Cl Species and Synthesis of Optically Pure (R_P)-(–)-Menthyl H-Phenylphosphinate

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Phenyl dichlorophosphine reacted with (*L*)-(–)-menthol to afford two diastereomers of menthyl phenylphosphinate (R_P)-**1a**/(S_P)-**1a**′ in up to 89:11 *dr*. Compound (R_P)-**1a** was isolated in 58 % yield (60 g) and > 99:1 *dr*. An HCl-promoted diastereoselective hydrolysis of the P–Cl species was found to be involved in the reaction. On the basis of this, a mixture of **1a**/**1a**′ with 50:50 *dr* was converted to a mixture enriched in **1a** with 88:12 *dr* by treatment with phosphorus trichloride.

Introduction

P-Stereogenic phosphorus compounds are of high importance either as biologically active substances or as precursors of chiral phosphine ligands that are widely used in asymmetric catalysis.[1] However, acquisition of these compounds in optically pure form usually involves tedious processes such as kinetic resolution or the use of chiral auxiliaries. Although the configuration at the phosphorus center can be completely retained or inverted during some reactions, the initial generation of a chiral phosphorus atom often gives unsatisfactory stereoselectivity,[2] which results in bottlenecks in the preparation and application of P-stereogenic compounds.

As relatively easily accessible compounds, chiral P–H species attract considerable attention because of their various applications in the construction of P–C bonds[3] through cross-coupling, substitution, or hydrophosphinylation.[4] Among chiral P–H species, (R_P)-(–)-menthyl phenylphosphinate (**1a**) is very commonly used due to the ease with which various groups such as alkyl, vinyl or aryl can be effectively introduced onto the chiral phosphorus atom. Recently we reported the addition of **1a** to C=O bonds to form P-stereogenic α-hydroxy phosphinates.[5a,5b] Also, optically pure **1a** was used as precursor of P-stereogenic secondary phosphine oxides,[5c] or directly as a ligand for asymmetric hydrogenation.[6]

A diastereomeric mixture of menthyl phenylphosphinate (R_P)-**1a**/(S_P)-**1a**′ was first prepared by Letsinger and co-workers from the reaction of $PhPCl_2$ with (*L*)-(–)-menthol, followed by hydrolysis of the intermediate with water.[7] Mislow and co-workers obtained a mixture enriched with **1a** (**1a**/**1a**′ ca. 95:5) by fractional recrystallization.[8] Thereafter, several preparations and applications of the compound were reported.[4,9] Furthermore, **1a** and analogues have been obtained by the treatment of $MenOPCl_2$ with aryl Grignard reagents, followed by hydrolysis, resulting in yields of around 30% of the diastereomerically pure product.[5,6,10] Recently, Berger and Montchamp reported a multi-step strategy to prepare **1a** starting from hypophosphorous acid, paraformaldehyde, and (–)-menthol.[11] A straightforward and practical method suitable for the preparation of optically pure P–H species in satisfactory yield and on a ten-gram scale has scarcely been developed.

When following Mislow's procedure,[5] we found optically pure **1a** (> 99:1) could be obtained, but in quite poor yield. Meanwhile, a mother liquor that contained **1a**/**1a**′ in near 1:1 *dr* was obtained. The yield of **1a** depended upon the *dr* of **1a**/**1a**′ when the two diastereomers were formed by the hydrolysis of the intermediate P–Cl species. To the best of our knowledge, the hydrolysis of such asymmetric P–Cl species, including the stereochemistry and improvement of the ratio of the two produced stereoisomers, has not been reported in detail. Herein, we endeavored to reveal the mechanism and thus to improve the ratio of **1a**/**1a**′.

Results and Discussion

In the presence of pyridine, (*L*)-(–)-menthol reacted with $PhPCl_2$ to form menthyl phosphorochloridite **2a**. Hydrolysis of **2a** in situ at low temperature selectively afforded **1a** and its epimer **1a**′. As seen in Table 1, the best *dr* (85.5:14.5) was obtained from the hydrolysis with water (Table 1, entry 1). Acidic, alkaline, and alcoholic additives for the hydrolysis resulted in a decreased *dr* (Table 1, entries 4–7). A poor *dr* was also observed when excess $PhPCl_2$ was used

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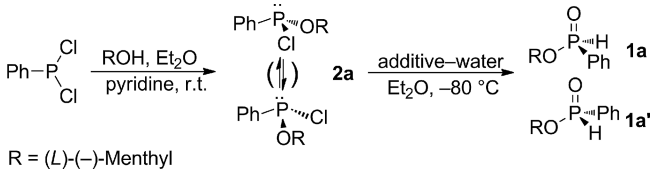
(Table 1, entries 2–3); in these cases more than 1 equiv. of HCl was generated during hydrolysis. When ethanol was used as an additive, free (*L*)-(–)-menthol was detected, which was probably formed from replacement of menthoxyl with ethoxyl.

Table 1. Formation of **1a/1a′** from $PhPCl_2$ and (*L*)-(–)-menthol.



R = (*L*)-(–)-Menthyl

Entry	Amount of $PhPCl_2$	Additives	**1a/1a′**[a]
1	1.2	–	85.5:14.5
2	1.8	–	80:20
3	2.4	–	77:23
4	1.2	acetic acid	80:20
5	1.2	ethanol	71:29[b]
6	1.2	pyridine	50:50[c]
7	1.2	conc. HCl	81:19

[a] The **1a/1a′** ratio was estimated by ^{31}P NMR spectra. [b] Free menthol was detected in 40%. [c] An unconfirmed compound with a peak at δ = 26.89 ppm in the ^{31}P NMR spectra was formed in 25% yield.

Pure **2a** could be isolated by distillation.[12] Two single peaks at δ = 175.14 and 178.15 ppm, in the ratio of 1:1, were observed on its ^{31}P NMR spectra, which were assigned as the two diastereomers derived from the *R* or *S* configuration at phosphorus. Hydrolysis of isolated **2a** confirmed the dependence of *dr* on solvents, temperature, and other conditions. As shown in Table 2, better selectivity was obtained in diethyl ether. Either less or more polar solvents than diethyl ether such as pentane, toluene, chloroform, and THF, gave poorer *dr*. In diethyl ether, a 72:28 *dr* was obtained at room temperature, and a higher *dr* of 89:11 was obtained at –90 °C (Table 2, entries 7 and 9). The replacement of water with aqueous THF for the hydrolysis clearly did not improve the *dr* (Table 2, entries 9 and 10).

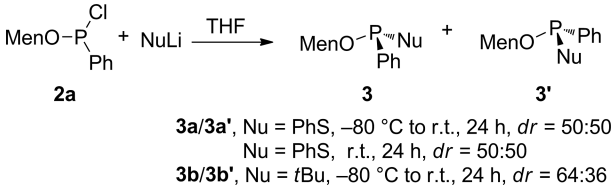
Table 2. Hydrolysis of menthyl phosphorochloridite **2a**.

Entry	Solvent	*T* [°C]	Ratio of **1a/1a′**[a]
1	Pentane	25	63:37
2	Toluene	25	54:46
3	Toluene	–90	68:32
4	$CDCl_3$	25	63:37
5	$CDCl_3$	–80	61:39
6	THF	–80	71:29
7	Et_2O	25	72:28
8	Et_2O	–80	87:13
9	Et_2O	–90	89:11
10	Et_2O	–90	88:12 [b]
11	Et_2O/pentane	–90	79:21
12	Et_2O/HMPA	–90	57:43
13	Et_2O/Et_3N	–90	66:34 [b]

[a] The **1a/1a′** ratio was estimated by ^{31}P NMR spectra. [b] A mixture of THF/water was used.

The reaction of $PhPCl_2$ with (*L*)-(–)-menthol on a 0.37 mol scale was carried out at –80 °C, and two diastereomers **1a/1a′** were formed in 80:20 *dr*. On this scale, **1a** was isolated in 58% yield (60 g) from recrystallization with hexane at –30 °C. Meanwhile, the mother liquor that contained **1a/1a′** (ca. 1:1) was obtained in 39% yield. Total yield of **1a**, together with **1a/1a′**, was near to quantitative. Attempts to isolate (S_P)-**1a′** failed. It was clear that the isolated yield of (R_P)-**1a** depended on the original ratio of **1a/1a′**.

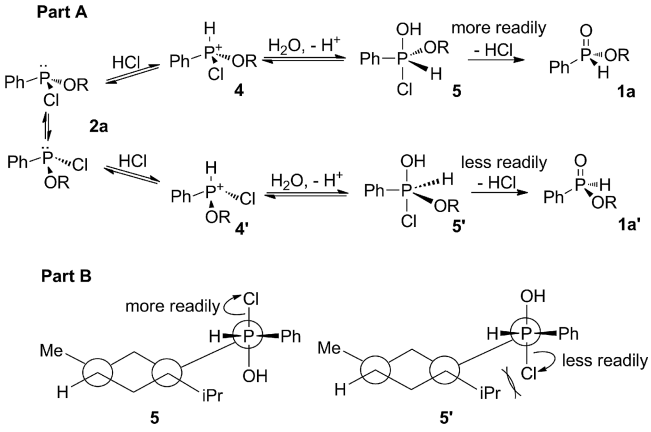
Although the mechanism for hydrolysis of **2a** remained unclear, we can speculate some aspects based on the appearance of the reaction. Initially, **1a** and **1a′** were thought to be directly formed from two stereoisomers of **2a**, respectively. However, the 1:1 ratio of two peaks of **2a** in the ^{31}P NMR spectra, even at low temperature (–78 °C), indicated that neither one of the two stereoisomers was dominant. Capturing **2a** also confirmed this observation. When PhSLi was added to the solution of **2a**, either at room temperature or at –80 °C, *O*-menthyl *S*-phenyl phenylphosphonothioite **3a/3a′** was obtained in the ratio of 1:1, which was confirmed by the equal heights of peaks at δ = 146.7 and 150.5 ppm in the ^{31}P NMR spectrum (Scheme 1). When *tert*-butylmagnesium chloride was used, a mixture of *tert*-butyl(menthoxy)phenylphosphine **3b/3b′** was obtained in a ratio of 64:36. The slight selectivity may be ascribed to the steric hindrance of the bulky *tert*-butyl group. These results demonstrated that **1a/1a′** were not formed directly from the two stereoisomers of **2a**.



Scheme 1. Confirmation the diastereomeric ratio of **2a** at low temperature.

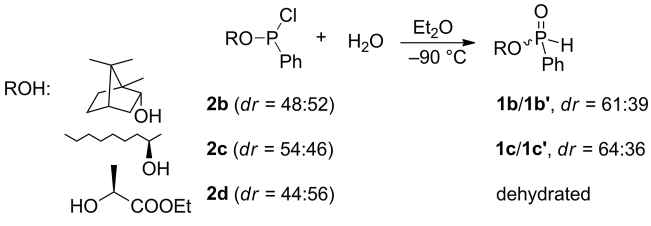
The poor *dr* for hydrolysis of **2a** with water–alkali additives (Table 1, entry 6, Table 2, entry 13) indicated that simultaneously formed HCl was necessary for the selective formation of **1a**. As shown in Scheme 2, we supposed that HCl combined with **2a** to form quaternary phosphonium salt **4/4′**, which was attacked by nucleophilic water, via a possible five-coordinate phosphorus intermediate **5**, to afford **1a/1a′**. The chloride anion tended to leave from an axial position of the trigonal bipyramidal **5/5′**. As seen in Scheme 2, b, loss of the chloride anion from **5** was less hindered by the bulky *ortho*-isopropyl group than in **5′**, which would result in **1a** being formed predominantly.

More than 1 equiv. of HCl tended to combine with water to form H_3O^+ and reduce its nucleophilic activity, which would hinder the formation of **5/5′**. At low temperature (–80 °C), water will be solidified quickly. Due to the limited solubility of water in ether, the presence of excess HCl would lead to incomplete hydrolysis of **2a** at low temperature, and give poor **1a/1a′** ratio (Table 1, entries 1–3 and 7).



Scheme 2. Proposed mechanism for hydrolysis of **2a**.

Various chiral alcohols were examined for the preparation of P-stereogenic phenylphosphinates by a similar procedure. However, only (*L*)-(–)-menthol gave satisfactory selectivity. The corresponding phosphorochloridites **2b**, **2c**, and **2d** were obtained from borneol, (*R*)-nonan-2-ol, and (*S*)-ethyl 2-hydroxylpropanoate, respectively. Hydrolysis of **2b** and **2c** in diethyl ether gave **1b** and **1c** in around 60:40 *dr* (Scheme 3). During hydrolysis of **2d**, dehydration elimination occurred and ethyl acrylate was formed as the major product.



Scheme 3. Hydrolysis of **2** derived from various chiral alcohols.

On the basis of the well-known equilibrium between hydrogen phosphinate P(=O)–H and phosphonite P–OH, the latter can be converted to P–Cl species by triaryldichlorophosphorus or phosphorus trichloride.[13] We hoped the mixture of **1a/1a′** could be converted to **2a** by phosphorus trichloride,[14] which could afford **1a** predominantly when hydrolyzed at low temperature, as above.

The conversion of **1a/1a′** (1:1) to a mixture enriched in **1a** under different conditions was examined (Table 3). As seen in entries 1 to 3, 1 equiv. of PCl_3 was essential. An inadequate amount of PCl_3 resulted in incomplete conversion of **1a/1a′** to **2a**. The best *dr* was obtained from a slight excess of PCl_3 (1.2 equiv.). It was necessary to remove HCl immediately with pyridine (Table 3, entries 4, 8 and 9). Excellent selectivity was obtained when 1 or 2 equiv. of pyridine was used (Table 3, entries 5–6). In the presence of 3 equiv. of pyridine, the selectivity was completely lost, since all the HCl was neutralized (Table 3, entry 7), which was similar to the above hydrolysis by water–alkali additive (Table 1, entry 6 and Table 2, entry 13).

Table 3. Conversion of **1a/1a′** (1:1) to enriched **1a**.

Entry	**1**/PCl_3 (**1a/1a′** = 50:50)[a]	PCl_3/pyridine[a]	**1a/1a′** [b]
1	1:1.2	1:1	88:12
2	1:0.8	1:1	85.5:14.5
3	1:0.4	1:1	79:21
4	1:1.2	1:0	76:24
5	1:1.2	1:1	86:14[c]
6	1:1.2	1:2	85:15[c]
7	1:1.2	1:3	45:55[c]
8	1:1.2	1:0	54:46[d]
9	1:1.2	1:0	68:32[e]

[a] Molar ratio. [b] The ratio of **1a/1a′** was estimated by ^{31}P NMR spectra. [c] PCl_3 reacted with **1a/1a′** for 5 h at room temperature. [d] The reaction was carried out in dichloromethane. [e] The reaction was carried out in THF.

Conclusions

In summary, P-stereogenic *H*-phosphinate **1a** was prepared directly from commercially available (*L*)-(–)-menthol. The presence of 1 equiv. of HCl was necessary for the diastereoselective hydrolysis of the P–Cl species, but excess HCl resulted in decreased selectivity. The by-produced **1a/1a′** mixture can be used for the isolation of **1a** by treatment with PCl_3 then hydrolysis at low temperature. Our study provided a practical and straightforward method for preparation of optically pure H–P species that are widely used in asymmetric catalysis.

Experimental Section

Typical Procedure to Study the Selectivity for the Formation of 1a: Phenyl dichlorophosphine (0.52 mL, 3.85 mmol) was added to an ice-cooled solution of (*L*)-(–)-menthol (0.5005 g, 3.21 mmol) and pyridine (0.26 mL, 3.21 mmol) in dry ether (10 mL), under an atmosphere of nitrogen. The mixture was stirred at room temperature for 4.5 h then cooled to –80 °C. Water-saturated diethyl ether (20 mL) was added dropwise, and the mixture was stirred at –80 °C for 4 h. Saturated aqueous $NaHCO_3$ solution was added to the mixture and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layer was dried with anhydrous $MgSO_4$. After removing the solvents in vacuo, the residue was obtained as a colorless oil and was analyzed by ^1H and ^{31}P NMR spectroscopy. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (d, J = 552 Hz, 0.16 H), δ = 7.64 (d, J = 552 Hz, 0.84 H) ppm. ^{31}P NMR ($CDCl_3$, 300 MHz): δ = 25.23 (s, 83%), 21.83 (s, 17%) ppm.

Typical Procedure for the Hydrolysis of 2a: Water (5 μL) was added to a liquid nitrogen–diethyl ether-cooled solution (–90 °C) of **2a** (50 μL) in diethyl ether (1 mL). The mixture was stirred at the same temperature for 5 h, then warmed to room temperature and washed with water three times. After removing the solvent, the residue was analyzed by NMR spectroscopy. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (d, J = 552 Hz, 0.11 H), δ = 7.64 (d, J = 552 Hz, 0.89 H) ppm. ^{31}P NMR ($CDCl_3$, 300 MHz): δ = 25.23 (s, 89%), 21.83 (s, 11%) ppm.

Preparation of Optically Pure 1a: A solution of (*L*)-(–)-menthol (57 g, 0.37 mol) and pyridine (30 mL, 0.37 mol) in dry diethyl ether (250 mL) was added dropwise to an ice-cooled solution of phenyl dichlorophosphine (50 mL, 0.37 mol) in dry diethyl ether (250 mL), under a nitrogen atmosphere. The mixture was stirred at room temperature for 6 h, and then cooled to –80 °C. At this stage, the reac-

tion vessel can be opened to the air. Diethyl ether (500 mL, commercially available without purification) was added, followed by addition of water (15 mL), the mixture was stirred at –80 °C to room temperature overnight. Water (500 mL) was added and the organic layer was washed with water three times (3 × 400 mL). After drying over anhydrous $MgSO_4$ and removing solvents in vacuo, a colorless oil (100 g, 97% yield) was obtained, with 80:20 *dr* of **1a**/**1a′**. The crude product was recrystallized from pentane (100 mL, commercially available without purification) at –30 °C to afford a white solid (70 g) in 90:10 *dr*, which was recrystallized three times in pentane with a reducing temperature gradient from 20 °C to –30 °C to afford optically pure **1a** (first crop 15 g, second crop 40 g, and third crop 5 g, in total 60 g, 58% yield) with > 99:1 *dr*. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.64 (d, J = 552 Hz, 1 H), 7.74–7.79 (m, 2 H), 7.47–7.59 (m, 3 H), 4.22–4.31 (m, 1 H), 2.14–2.22 (m, 2 H), 1.64–1.70 (m, 2 H), 1.41–1.47 (m, 2 H), 1.18–1.27 (q, J = 12 Hz, 1 H), 0.98–1.09 (dq, J1 = 3.2 Hz, J2 = 12.8 Hz, 1 H), 0.95 (d, J = 7.2 Hz, 3 H), 0.89 (d, J = 6.8 Hz, 3 H), 0.85 (d, J = 6.4 Hz, 3 H), 0.81–0.91 (m, 1 H) ppm. ^{31}P NMR ($CDCl_3$, 300 MHz): δ = 25.28 (s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 133.07, 133.05, 130.86, 130.75, 128.92, 128.78, 79.17, 79.10, 77.58, 77.26, 76.95, 48.97, 48.91, 43.72, 34.15, 31.85, 26.01, 23.18, 22.05, 21.17, 15.97 ppm.

Typical Procedure for the conversion of 1a/1a′ to the Product Enriched in 1a: Phosphorus chloride (38 μL, 0.441 mmol) and pyridine (36.5 μL, 0.441 mmol) were added, in turn, dropwise to a solution of **1a**/**1a′** (102.8 mg, 0.367 mmol, ca. 1:1 *dr*) in diethyl ether, under nitrogen. The mixture was stirred at room temperature for 2 h, and then cooled to –80 °C. Water-saturated ether (5 mL) was added dropwise and the mixture was stirred at –80 °C for 4 h. After warming to room temperature, the mixture was washed with water twice and dried with anhydrous $MgSO_4$. After removing the solvents in vacuo, the residue was obtained as a colorless oil and was analyzed by ^{1}H and ^{31}P NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (d, J = 552 Hz, 0.12 H), δ = 7.64 (d, J = 552 Hz, 0.88 H) ppm. ^{31}P NMR ($CDCl_3$, 300 MHz): δ = 25.23 (s, 88%), 21.83 (s, 12%) ppm.

Acknowledgments

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